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In an attempt to select an appropriate fire-resistant hydraulic fluid for use in Naval applications two approaches were used (1) development of a shear-resistant drag reducing colloid dispersion presumed to be anti-misting and (2) use of water-in-oil emulsion loaded to high levels of water. While the dispersion of lithium phenylstearate colloid had demonstrated high drag reducing activity in previous work, it failed to produce the desired anti-misting effect characteristic of drag reducing agents at concentrations of 0.25, 0.50 and 1%. The water-in-oil emulsion, on the other hand, showed promising fire-resistant properties in a flammability testing device.

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FIRE RESISTANT HYDRAULIC FLUIDS

J. B. Romans* and R. C. Little

I INTRODUCTION

It is common knowledge that many materials not dangerously flammable in bulk, may be ignited explosively if they are finely divided. If the material is in liquid form, the situation becomes more critical, for fine mist can readily form if liquid under high pressure is suddenly released into the atmosphere through a small orifice or crack. Such a state may develop in hydraulic fluid systems because of suddenly stressed components aboard ships or aircraft brought on by exposure to combat, accident, vibration or other causes. If the liquid is an oil, a spark or other source of ignition is all that is required to generate a catastrophic explosion such as occurred on the USS BENNINGTON in 1954. It is well known that Mil-H-5606 hydraulic fluids are hazardous in this respect and even the less flammable MIL-H-83282 fluids may possibly be ignited if they are released into the atmosphere in the atomized state.

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It has been shown[1] [2] that it is possible to reduce the nature and extent of a "fire-ball" from atomized jet aircraft fuels by dissolving certain high molecular weight chemical polymers in the fuel. For example, polyisobutylene is an effective anti-misting fire suppressive agent for jet fuels[2] as well as for 2190-TEP hydraulic oil.[3] The polymer suppresses the formation of mists by increasing the size of the droplets. However, for anti-misting jet fuels to be utilized successfully by the engines, the anti-misting properties of the fuel must be decremented before combustion takes place.[4] The chemical polymers are very sensitive to shearing forces and are degraded by the action of pumps, screens, valves, etc., in aircraft hydraulic and fuel systems.[5] This property is suitable for a once-through system but not for a recirculating one such as a hydraulic system. Thus the chemical polymer type anti-misting agents would be short lived in hydraulic systems with their shear generating pumps, screens etc., and would therefore be unsuitable. For this reason no additional work has been done at NRL with polyisobutylene or similar polymers as anti-misting agents for hydraulic fluids.

Earlier reports[5] [6] have shown that "association" colloid type materials, such as the organo-metallic oil soluble polar compounds used in drag reduction studies are relatively shear resistant especially when compared with the chemical polymer polyisobutylene.[5] It has been suggested[5] [6] that the shear resistance of these polar materials arises from the ability of the molecules to restructure themselves through associative processes. Work with the May aerosol generator[7] has demonstrated that the association colloids significantly increase the average drop size for oils containing them from that observed with ordinary oils of the same viscosity. Even though this behavior is considered critical in the development of anti-misting fire-resistant fluids, final evaluation of the organometallic compounds rests on their behavior in flammability tests. Such tests of two oils of widely differing viscosities and containing lithium phenylstearate have been included in this study.

A number of non-hydrocarbon materials have been developed as fire resistant fluids.[8] These include an organo phosphate, silicate and phosphate esters, silicones and halocarbons, especially those containing fluorine. Many of these fluids will require modification of the systems in which they would be used in order to assure compatibility with the elastomers and metals involved. The problem of toxicity, particularly with the phosphates and the halocarbons and their reaction products, is of concern.

Water-containing materials, as emulsions or solutions, have been developed as fire-resistant or "nonflammable" fluids. Experiences with fire in the hydraulic systems of military equipment during and after World War II led to the development of the "Hydrolubes".[9] These were based on ethylene glycol-water solutions containing additives for viscosity index improvement, wear prevention and corrosion inhibition. The Hydrolubes found limited applications, in part, because of problems arising from wear prevention and corrosion inhibition, particularly with certain metals.

Experience with the gylcol-water hydraulic fluids suggests that the absence of an oil phase in the fluids seriously limited their ability to compete with petroleum oils. However it had been determined[9] that at least 40% by volume of water is required to prevent the propagation of flames in liquid spray in the atmosphere. This suggests that a stable pumpable emulsion of water and oil might provide both the fire resistance desired and the lubricating qualities of petroleum type hydraulic oils. Work in this field does not appear to be very extensive. However, recent developments[10] in "nonflammable" water-in-oil emulsions have shown promise for use in hydraulic systems of mining machinery. The flammability of one of these fluids containing 41% water has been investigated with promising results.[10]

II EXPERIMENTAL

Materials

The fluids studied were petroleum type 2190-TEP hydraulic oil (Mil-L-17331F Ships 1973); experimental fluids consisting of petroleum type aircraft turbine engine oil (Mil-0-6081B (ASG) and AM.4) containing lithium phenylstearate as a thickening agent in nominal concentrations of 0.25%, 0.5% and 1%; a fluid made up of equal parts of 2190-TEP hydraulic oil and 1005 aircraft oil containing 0.5% lithium phenylstearate; and a water-in-oil emulsion, Mobil XRL 1262, supplied by Mobil Research and Development Corp, Paulsboro, N. J. The significant comparable properties of 2190-TEP hydraulic oil, 1005 aircraft oil, and Mobil XRL 1262 hydraulic fluid are given in Table I. The chemical and physical properties of the fluids containing lithium phenylstearate were not determined pending indication of the usefulness of the stearate as an anti-misting agent.

The lithium phenylstearate additive was dispersed in the 1005 oil by first dissolving it in a 50-50 mixture of benzene and isopropanol at 80°C after the method used in earlier work.[5] A small amount of the 1005 oil was added and the mixture heated to 150°C to evaporate the solvents. When a thickening of the mixture occurred, the remainder of the 1005 oil required was added to the concentrate. More dilute solutions were then made by adding additional 1005 oil or 2190-TEP hydraulic oil, depending on the mixture desired.

Apparatus

A spinning disk atomizer was used to measure the mist flammability of hydraulic oils. The disk, patterned after one used by Mannheimer[11] with aircraft jet fuels, was made of brass and measured 4 1/4 inches in diameter and 1/2 inch in thickness. It contained a cavity in the center, 1 inch in diameter and 1/4 inch deep. Four radial holes 0.149 inches in diameter and spaced 90° apart were drilled from the rim of the disk into the cavity. In operation, fluid delivered to the cavity while the disk was spinning was dispensed by centrifugal force through the radial holes in the form of a mist.

The disk was mounted on the vertically oriented shaft of the drive motor as shown in the schematic diagram in Figure 1. Two types of motors were used; a GAST air motor (10,000 rpm, max.) or an AMETEK high speed series type electric motor capable of operating up to 22,000 rpm. A variable pressure reducing valve was used to control the speed of the air motor and a variable autotransformer was used to control the speed of the electric drive motor. Speed of the spinning disk was measured by a PIONEER DT-36 digital photoelectric tachometer with a remote pickup which focused on a piece of reflective tape attached to the surface of the spinning disk. The source of ignition of the fluid mist was a propane burner located 8 inches from the center of the spinning disk and at the same level.

The spinning disk and drive motor were mounted on a tubular pedestal, bolted to a heavy steel base plate, and, with the propane burner, the entire assembly was placed in the center of an open-top rectangular cinder-block enclosure measuring 4 1/2 by 5 1/2 feet. The spinning disk atomizer using the electric motor drive is shown in Figure 2. A camera was used to record the flammability characteristics of the various fluids under study.

The hydraulic oil was delivered to the spinning disk from a safe distance through 1/2 inch diameter copper tubing by means of a low shear positive displacement syringe or pump, consisting of a vertically mounted cylinder and movable piston. A schematic of the arrangement of the syringe and accessories are included in Figure 1. The cylinder measured 5 1/4 inches in diameter and 5 1/4 inches long. Displacement of the fluid was accomplished by moving the piston at a very slow rate by a lead screw driven by a gear motor through a variable ratio speed reducer. Speed of the gear motor was controlled by a HELLER Model S-30 motor control unit and was monitored by a recorder driven by a DC generator coupled to the gear motor. Limit switches on the lead screw determined the length of travel of the piston. The volume of fluid displaced during a single stroke of the piston was approximately 1470 ml. Means were provided whereby the fluid delivery line could be purged with compressed air when charging the system with a new fluid.

Procedure

Unless the fluid to be tested was the same as that used in the previous determination, the fluid delivery line was purged by opening the air valve on top of the syringe cylinder. The filler plug was then removed and the piston lowered to the bottom of the stroke. The cylinder was then charged with the new fluid and the plug replaced.

It has been found beneficial in terms of disk speed stability, especially when the air drive motor is used, to operate it at half speed for several minutes while preparing for the first test of the day. The propane burner was then ignited, the disk drive motor brought up to the desired speed, usually 10,000 rpm, ± 2%, and allowed to stabilize for a few minutes. If it was anticipated that the fluid under test would ignite, the tachometer remote pick-up was removed to prevent damage to the unit. After the camera was in place, the syringe drive motor was started. For work with hydraulic oils, fluid delivery rates of both 400 ml/min and 850 ml/min were used.

As the fluid entered the cavity in the center of the spinning disk, the disk speed was reduced (12%-13% at 400 ml/min delivery and 21%-23% at the 850 ml/min level) because of the centrifugal force required to disperse the fluid from the spinning disk. At this point, the operator had the option of restoring the disk speed or of raising the speed an appropriate amount before the test fluid was admitted to the disk. In either case, the same procedure was followed for a series of tests for, in general, it has been found that higher disk speeds tended to increase the flammability of the fluid under test. This is due to the formation of smaller droplets at the higher disk speeds for

(3)

a given fluid. Similar behavior has been observed with the May spinning disk aerosol generator.

Any propagation of yellow flame from the blue propane flame was considered evidence of ignition of the fluid under test. An arc of flame was established which sometimes completely encircled the spinning disk. The degree of encirclement at a given disk speed and fluid delivery rate was a qualitative indication of the relative flammability of the fluid. The flame could be extinguished by stopping the syringe drive motor. If there was no propagation of flame from the propane flame, the fluid under test was considered to be fire resistant.

III RESULTS AND DISCUSSION

The results of the flammability studies are summarized in Table II.

The flammability of 2190-TEP hydraulic oil in mist form was readily demonstrated in the flammability apparatus. At a fluid delivery rate of 400 ml/min, and an initial disk speed of 8,900 rpm with the air motor drive, ignition occurred and a 90°-120° arc of flame was established. Figure 3 is typical. When the fluid delivery rate was increased to 850 ml/min, the arc of flame increased to about 180° as shown in Figure 4. However, if the disk speed was maintained at a nominal 10,000 rpm during the run, the flame completely encircled the spinning disk (Figure 5). This was due to the decrease in droplet size at the higher disk speeds as mentioned earlier.

The 1% lithium phenylstearate in 1005 aircraft oil appeared to be too viscous to pass through the radial holes in the spinning disk. Instead, strings or globules of the mixture were thrown off the top of the disk, even when the fluid delivery rate was reduced from 400 ml/min to 200 ml/min. When the material intercepted the propane flame, it ignited rapidly resulting in an irregular arc of flame at about 120° or more. The poor performance of the 1% lithium phenylstearate mixture led to the formulation of a 0.25% solution of the polymer in 1005 oil. The less viscous material was readily atomized by the disk at delivery rates of either 850 ml/min or 400 ml/min. However, with the disk operating at an initial speed of 10,150 rpm the stearate solution ignited at both delivery rates and formed a very intense flame which completely encircled the disk. The flame generated was quite reminiscent of that observed in earlier work with jet aircraft fuels.[2] The condition was not improved by increasing the stearate content to 0.5%. The delivery rate was limited to 400 ml/min and the initial disk speed was 10,150 rpm. Again ignition occurred and an intense flame was formed which encircled the spinning disk. In order to determine the effectiveness of the phenylstearate polymer in the 2190-TEP oil and to increase the viscosity of the 1005 oil solutions, a mixture consisting of equal volumes of 0.5 lithium phenylstearate in 1005 oil and 2190-TEP hydraulic oil was prepared. Using the same operating conditions as before, the composite mixture ignited readily in the flammability apparatus and formed an intense flame which completely encircled the spinning disk. The view in Figure 6 is typical of the flammability characteristics of all the mixtures containing 0.25% and 0.50% lithium phenylstearate.

The flammability apparatus fluid delivery system was purged of the previously used material and refilled with the water-in-oil Mobil XRL 1262. The flammability tests were conducted under the conditions found to be conducive to the ignition and flame propagation of 2190-TEP oil by maintaining a nominal 10,000 rpm disk speed during delivery of the fluid. Some luminuous scintillation effect occurred in the propane test flame, but no ignition occurred. Figure 7 is typical of the behavior of the Mobil fluid during several trials at a fluid delivery rate of 400 ml/min. No ignition occurred when the delivery rate was increased to 850 ml/min, but as can be seen in Figure 8, the flammability apparatus was engulfed in a dense fog of atomized emulsion. Such a condition with a flammable fluid would be expected to enhance the chances of ignition, but the Mobil XRL 1262 did not burn.

The vulnerability of 2190-TEP hydraulic oil in atomized form to ignition was well demonstrated by the flammability apparatus. A similar condition would arise as the result of a minute crack or break in a high pressure hydraulic system containing this material. To prevent this, either an anti-misting agent with shear resistant qualities and suitable for use with petroleum oil type hydraulic fluids will be required, or some other fire-resistant fluid is needed.

It seems obvious that even though lithium phenylstearate is useful as a drag reducing agent and has the ability to withstand shear stresses existing in hydraulic systems, it does not impart anti-misting properties to petroleum-type oils.

It is apparent that the mechanisms involved in drag reduction and shear-resistant properties are not the same as those exhibited by the anti-misting chemical polymer additives. Since the chemical polymers do not resist shear stresses well, more work will be required to formulate a shear resistant anti-misting additive for petroleum-type hydraulic oils.

The absence of ignition of the water-in-oil emulsion, Mobil XRL 1262 fluid, in the flammability apparatus despite the fact that it contains over 50% organic material, indicates its promise as a fire-resistant hydraulic fluid. It is seen from Table I that the pertinent physical and chemical properties are similar to those required for 2190-TEP oil. The pH of the emulsion is on the slightly alkaline side, a condition well known to inhibit the corrosion of steel. The pour point of -35°C exceeds that required of 2190 TEP oil, despite the 41% water content. Finally, the Mobil fluid as well as similar fluids[10] have been subjected to hydraulic pump tests to demonstrate anti-wear properties. These tests would also be indicative of the shear resistant properties of these fluids.

The effect of water in water-oil emulsion systems appears curious with respect to its effect on combustion characteristics. Dispersed water in oil in the range of 2 to 10 percent promotes combustion of many fuel types.[12] It essentially acts as an anti-knock additive boosting the octane number of the fuel. Such water may be ultrasonically dispersed immediately before combustion takes place or an emulsion may be prepared and stored for some time before use by employing small amounts of an emulsifier (surfactant) as an emulsion stabilizer. Water apparently acts in the following fashion:[13] As the emulsion droplet undergoes combustion, heat is tranferred from the surrounding diffusion flame to the drop. Sufficient superheating may occur so that the microdroplets of water contained within the oil droplet explosively vaporize causing the oil droplet to become highly fragmented and dispersed in the air phase. However, when surfactant is added in amounts above that required to stablize the emulsion, the water may become solubilized or microemulsions may possibly form. In this case the water does not promote improved combustion since it is apparently more intimately mixed with the combined oil and surfactant phases and less free to explosively superheat. It has been found, for example, that microemulsions of water in diesel fuel at the 10% level (stablized by 6% surfactant) gave fire-resistant properties in mist flammability experiments.[14]

The present emulsion tested in this report, containing 41% dispersed water and 5% surfactant, would therefore be expected to be fire-resistant a priori. The mechanism by which flames are propagated through fuel mists, however, are unknown at present. Moreover, the mechanism by which dispersed water within mists of emulsions acts to inhibit or prevent combustion would perhaps be even somewhat less understood. Clearly though, the heat involved in the combustion process is sufficient to greatly overwhelm the latent heat of vaporization of dispersed water - even at the 41% level (about 10,000 calories per gram versus - 539 calories per gram). That is, the latent heat of vaporization of the water itself is not sufficient to inhibit combustion. However, vaporization of the 41% water-in-the oil emulsion droplet would produce a vaporized mixture containing 7% oil and 93% water (excluding the oxidizing atmosphere). The high concentration of water molecules (approximately 14 water molecules per oil molecule, assuming a molecular weight of 350 for the oil) probably acts to a large extent as an inert diluent, reducing the oxygen concentration to below that required for propagation of the flame. Early work of the Bureau of Mines[15] and later work at NRL[16-18] have shown that hydrocarbon flames do not propagate at oxygen concentrations below 12-14%.

IV CONCLUSIONS AND RECOMMENDATIONS

The flammability problem known to exist with petroleum-type hydraulic oils in finely divided mist form has been demonstrated by the behavior of 2190-TEP hydraulic oil in the NRL flammability apparatus. It has been found that the association colloid, lithium phenylstearate, has no value as an anti-misting agent for use with petroleum oils. It is evident that the shear-resistant association mechanism effective in drag reduction phenomena is not that required for an anti-misting agent. It is recommended that the search for other materials be continued.

It has been found that the water-in-oil emulsion, Mobil XRL 1261, does not ignite in the NRL flammability apparatus. It shows promise as a potential substitute for petroleum oil type hydraulic oils now in use. It is recommended that additional studies of this and similar fluids be made to establish their suitability as hydraulic fluids for use in submarine hydraulic systems and for other Navy applications.

ACKNOWLEDGMENTS

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TABLE 1 - COMPARISON OF PROPERTIES OF FLUIDS STUDIED

Properties	2190-TEP Oil (a)	1005 Oil (b)	Fluid (c)
Flash point	400°F, min [1]	225°F, min [2]	—
Viscosity	82-110cs at 37.8°C(100°F) [3]	5cs, min at 37.8°C(100°F) [4]	110cs at 40°C
Pour Point	-6.7°C, max. (20°F) [5]	———	-35°C
Neutralization No. or pH	0.30, max [6]	0.100, max [7]	pH 8.1
Copper Corrosion	Slight tarnish permitted [8]	Slight brown stain permitted. [9]	pass [10]

1. ASTM Method D 92
2. Federal VV-L-791, Method 1103.5
3. ASTM Method, D 445
4. Federal VV-L-791, Method 305.2
5. ASTM Method D 97
6. ASTM Method D 974
7. Federal VV-L-791, Method 5105.3
8. ASTM Method, D 130
9. Federal VV-L-791, Method 5303.3
10. ASTM Method D 130-6

(a) Mil-L-17331F (Ships) 1973 requirements
(b) MIL-O-6081B (ASG) 1953 requirements
(c) Data supplied by manufacturer

TABLE II - FLAMMABILITY OF FLUIDS STUDIED

Fluid	Fluid Delivery Rate, ml/min 400	850	Disk Speed 10,000 rpm ±2% Initial	Maintained	Ignition	Circular Flame Projection
2190-TEP	x		x (8900)		Yes	90° - 120°
		x	x		Yes	180°
		x		x	Yes	360°
1% lithium phenyl-stearate in 1005 oil	x		x		Yes	120°
0.25% lithium phenylstearate in 1005 oil	x		x		Yes	360°
		x	x		Yes	360°
0.5% lithium phenylstearate in 1005 oil	x		x		Yes	360°
0.5% lithium phenylstearate in 1005 oil + 2190-TEP	x		x		Yes	360°
Mobil XRL 1262		x		x	No	-
	x			x	No	-

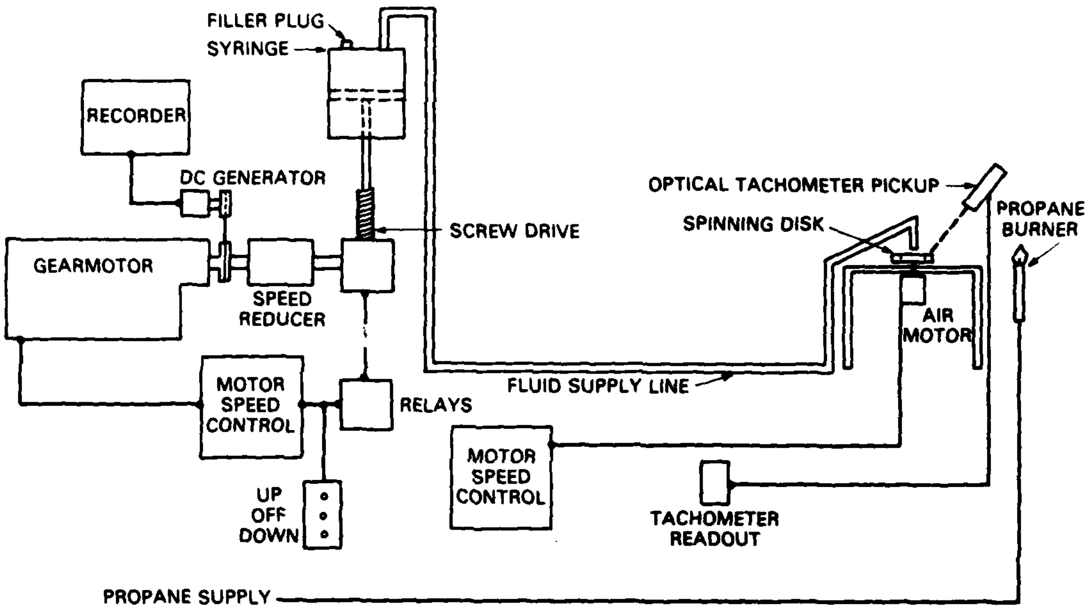

Fig. 1 — Schematic diagram of NRL flammability apparatus

Fig. 2 — The NRL spinning disk atomizer

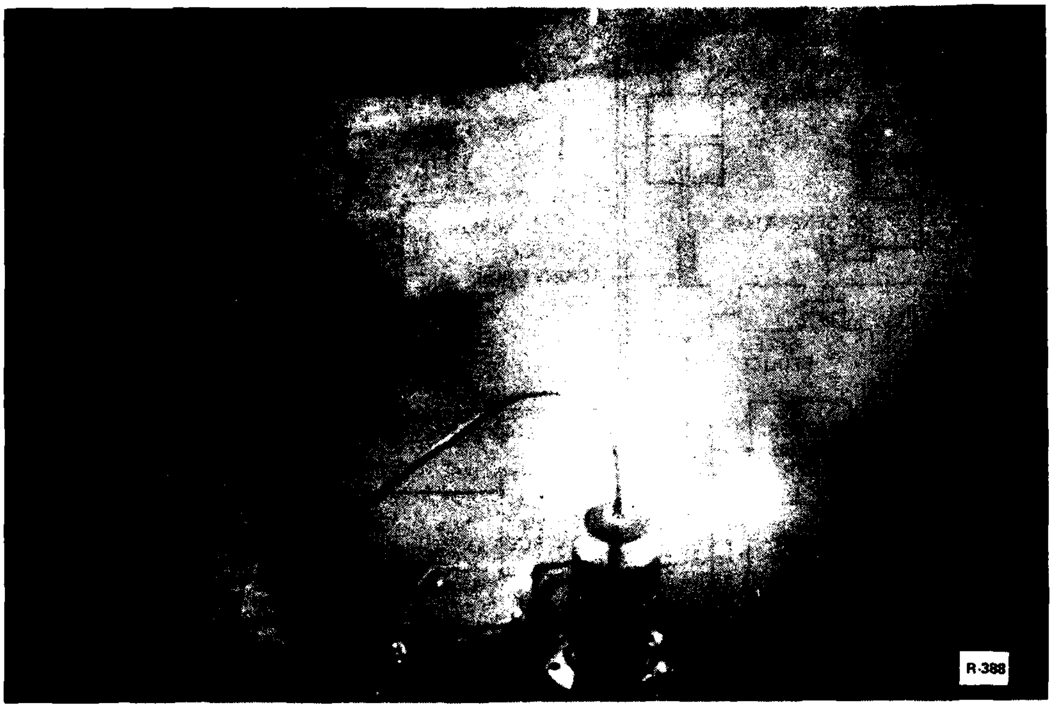

Fig. 3 — Typical behavior of 2190-TEP hydraulic oil in the NRL flammability apparatus

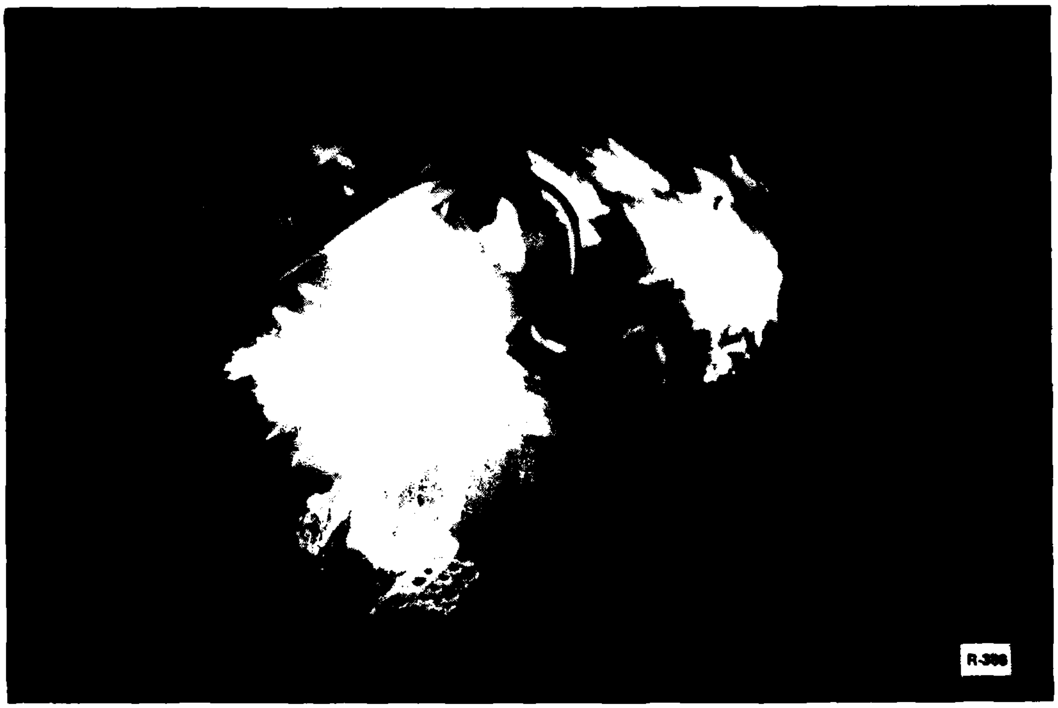

Fig. 4 — Effect of increased oil flow in the flammability of 2190-TEP hydraulic oil

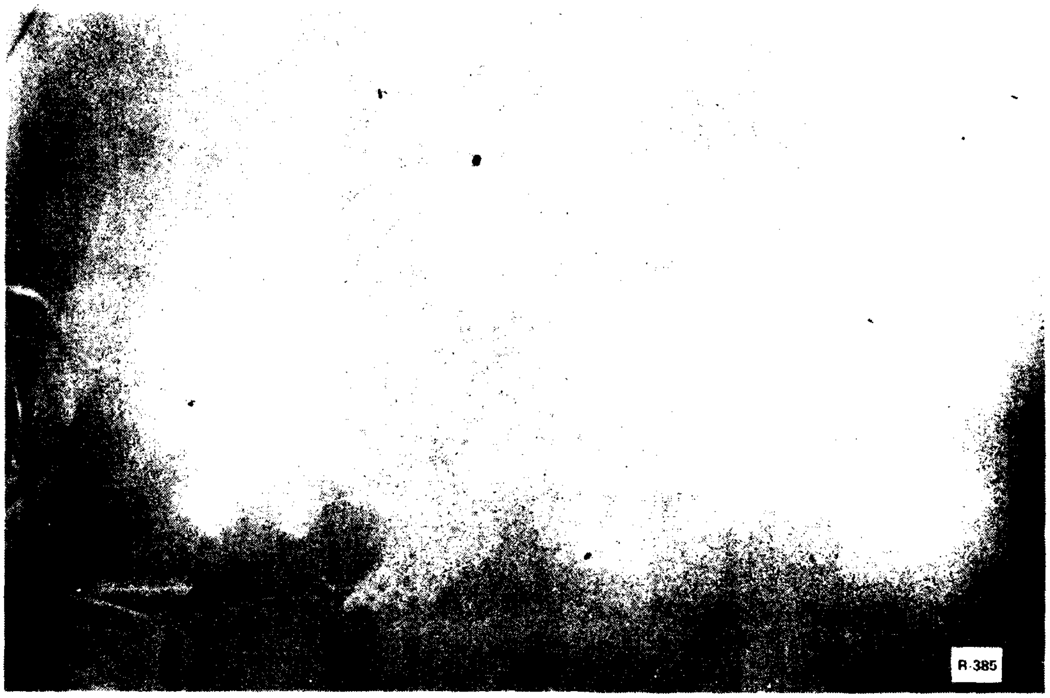

Fig. 5 — Increased disk speed intensifies burning of 2190-TEP hydraulic oil in the flammability apparatus

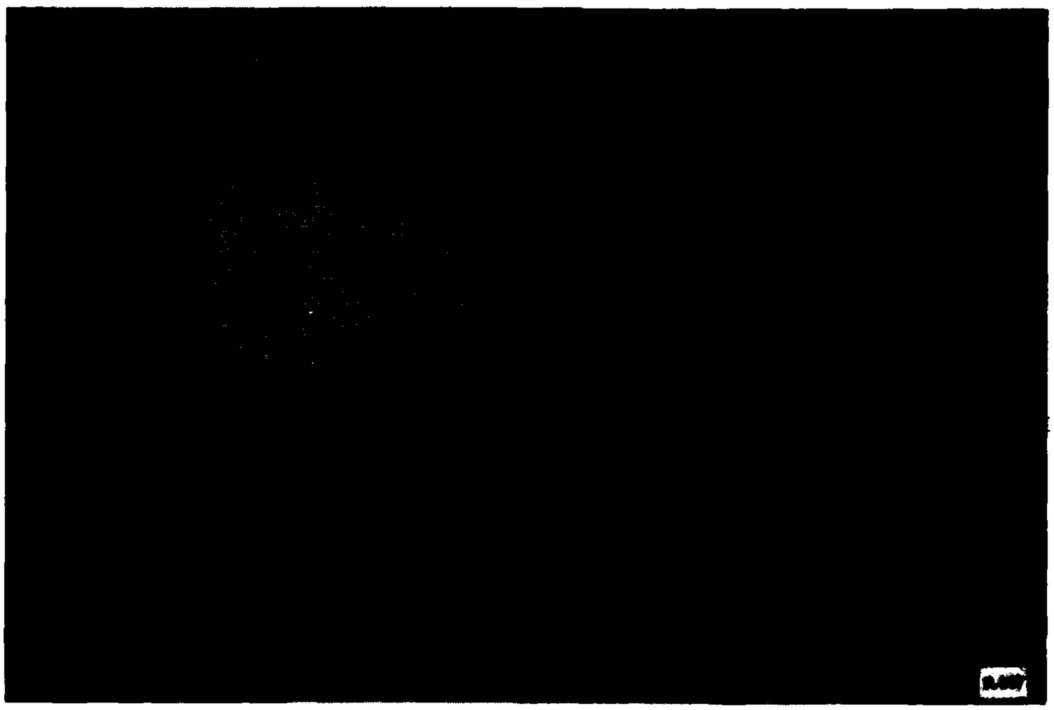

Fig. 6 — Fireball generated with the flammability apparatus by burning 1005 aircraft oil containing lithium phenylstearate

Fig. 7 — Demonstration of the nonflammability of Mobil XRL 1262 fluid in the NRL flammability apparatus

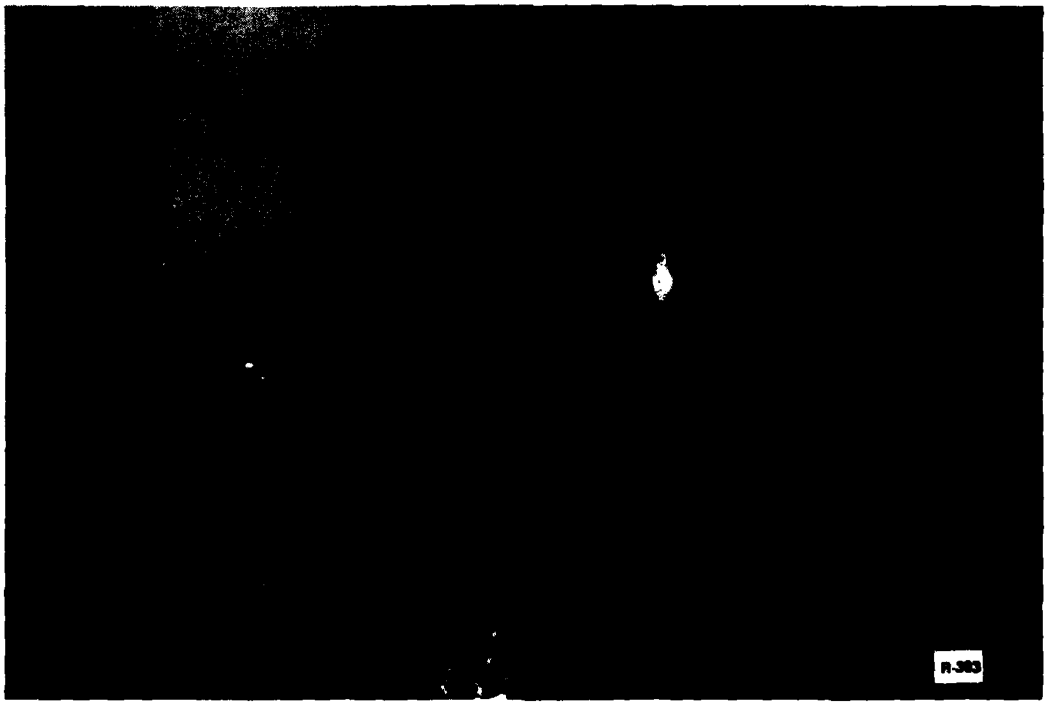

Fig. 8 — Fog generated by increased flow of Mobil XRL 1262 fluid fails to ignite in the NRL flammability apparatus

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